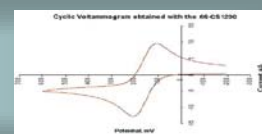


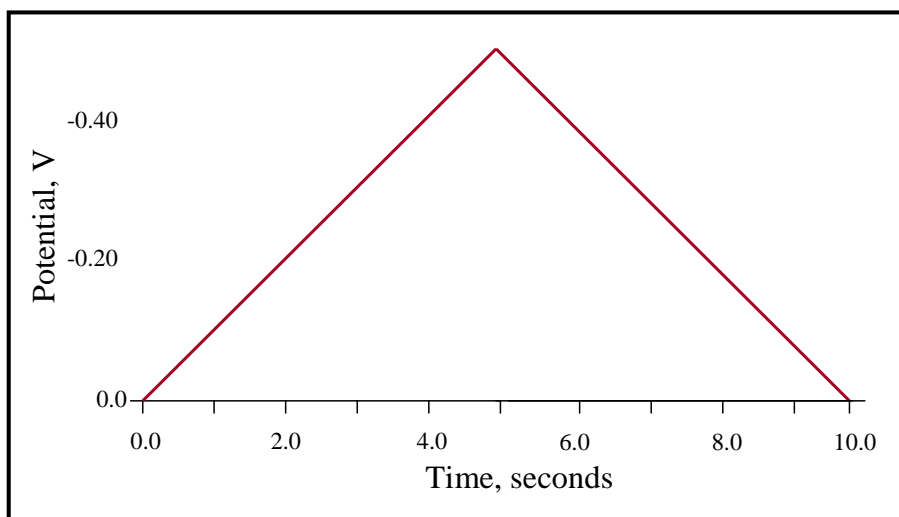
Analytical Electrochemistry: The Basic Concepts



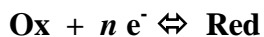
b) Cyclic Voltammetry

i) Introduction. In *linear scan voltammetry (LSV)*, the potential applied to a working electrode is scanned over some potential range of interest as a function of time, while the current passing at the electrode is measured. We saw in a previous section that the current – potential profile for LSV was peak shaped for an electroactive species undergoing an electron transfer reaction. In *cyclic voltammetry (CV)*, the potential scan is *reversed* at some point beyond the peak, and scanned back in the direction of the initial potential. In a simple CV experiment, the potential waveform applied to the electrode is a *triangle*, with the initial and final potentials being the same. This is illustrated in **Figure 17** for a scan between an initial potential of 0.00 V and a *switching potential* of -0.50 V, with a *final potential* of 0.00 V. For a scan rate of 0.10 V/s, the cycle takes 10.0 seconds to complete.

Figure 17



Remember that the reduction of an oxidized form (Ox) of a solution species at a solid electrode can be represented by



where n represents the stoichiometric number of electrons for the process, and *Red* represents the reduced form of the solution species. Under the appropriate conditions, this is the reaction that occurs on the forward scan in cyclic voltammetry. Now remember that the double-sided arrow indicates that the oxidized form of the solution species can be regenerated in a gross chemical sense from the reduced form (*chemical reversibility*), meaning that the product is stable on the

time scale of the voltammetric experiment. Upon reversal of the potential scan, the electrode in our example becomes more oxidizing and the oxidized form of the solution species can be *regenerated* from the reduced form now in the vicinity of the electrode as the potential moves through the region of the $E^{0'}$ for the redox couple. This oxidation reaction can be expressed by



The current – potential trace for a *chemically and electrochemically reversible* redox couple with an $E^{0'} = -0.30$ recorded between 0.00 and -0.50 V is shown in **Figure 18**. In essence, the *cyclic voltammogram* produced is the result of two separate *linear scan voltammograms*, one beginning at 0.00 V and ending at the switching potential of -0.50 V, and a second beginning at -0.50 V and ending at 0.00 V. (DigiElch simulation parameters: $\nu = 0.100$ V/s; $A = 0.050$ cm²; $C_i = 1.0$ mol/cm³; $D = 1.0 \times 10^{-5}$ cm²/s; $\alpha = 0.50$; $k_s = 100$ cm/s)

Figure 18

